

# Ionisation of $\text{H}_2$ in intense ultrashort laser pulses: parallel versus perpendicular orientation

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A theoretical comparison of the electronic excitation and ionisation behaviour of molecular hydrogen oriented either parallel or perpendicular to a linear polarised laser pulse is performed. The investigation is based on a non-perturbative treatment that solves the full time-dependent Schrödinger equation of both correlated electrons within the fixed-nuclei approximation and the dipole approximation. Results are shown for two different laser pulse lengths and intensities as well as for a large variety of photon frequencies starting in the 1- and reaching into the 6-photon regime. In order to investigate the influence of the intrinsic diatomic two-center problem even further, two values of the internuclear separation and a newly developed atomic model are considered.

**Keywords:** molecules in intense laser pulses; orientation-dependent ionisation; ultrashort molecular processes

## 1. Introduction

Despite the numerous experimental work on molecules in intense ultrashort laser pulses (see, e. g., (1) for a review) the theoretical treatment of even the simplest neutral molecule,  $\text{H}_2$ , remains a big challenge. In view of the interesting molecular strong-field phenomena like bond softening, bond hardening, or enhanced ionisation a deeper theoretical understanding of the molecular behaviour is desirable. This interest is further stimulated by recent progress in the direction of time-resolved molecular orbital tomography (2) or visualisation of nuclear dynamics with sub-femtosecond resolution (3–7). A key problem is the understanding of the relation of molecular structure on the strong-field response. There is, of course, the nuclear rotational and vibrational degrees of freedom them self which should be considered. Furthermore, even the purely electronic response of a molecule differs from the atomic one, since the electron density is anisotropic and depends on the nuclear geometry.

Only recently *ab initio* calculations for  $\text{H}_2$  exposed to strong fields became available in which both electrons are treated in full dimensionality. This includes calculations of the ionisation and dissociation behaviour of  $\text{H}_2$  exposed to an intense static or quasi-static electric field (8–13) which revealed the possible occurrence of bond softening and enhanced ionisation in *neutral*  $\text{H}_2$  due to a field-induced avoided crossing of the neutral ground state with the ion-pair state  $\text{H}^+\text{H}^-$ . Shortly thereafter, a full time-dependent calculation confirmed this finding (14–16). These calculations were based on a judiciously chosen grid on which the electronic wavefunctions were expanded. In a different approach the electronic wave-packet is expanded in terms of field-free eigenstates of  $\text{H}_2$  (17, 18). The same *ansatz*, but using a one-centre expansion for the electronic orbitals was used in (19). In that work even vibrational motion was included within the Born-Oppenheimer approx-

imation. All these works did, however, only consider a parallel orientation of the linear polarised laser field and the molecular axis. The reason is rather simple: in this case the problem of 6 spatial dimensions describing two electrons moving in the field of the laser and the two nuclei reduces effectively to a 5-dimensional one, because the quantum number of angular momentum along the molecular axis,  $M$ , is conserved or, equivalently, the cylindrical symmetry of  $H_2$  is not broken by the electromagnetic field.

Correspondingly, the consideration of the orientational dependence of the strong-field behaviour of  $H_2$  is rather limited so far. Within lowest-order perturbation theory (LOPT) a comparison of the ionisation rates for parallel and perpendicular orientation were presented for 2- and 3-photon ionisation and some internuclear separations in (20). More recently, the orientational dependence of  $H_2$  was also considered in full time-dependent treatments using either time-dependent density-functional theory (TD-DFT) (21) or a single-active electron approximation (SAE) (22). The validity of the SAE (and simplified models like the molecular Ammosov-Delone-Krainov tunnelling model (MO-ADK) or the molecular strong-field approximation (MO-SFA)) that reduces the problem to three spatial dimensions was recently investigated in (23). There it was found that especially in the few-photon case its applicability is quite restricted, since there is a pronounced dependence on the photon frequency due to the possible occurrence of resonantly enhanced multi-photon ionisation. Since the position of those resonances depends strongly on the excitation energies, a simplified model like SAE can lead to wrong positions of the resonances and thus a very wrong prediction for the ionisation rate at a given photon frequency.

In the present work the previously developed approach (17) for the full-dimensional *ab initio* treatment of the electronic motion in  $H_2$  exposed to an intense laser pulse was extended to the consideration of a perpendicular orientation of the molecular axis with respect to the field. This means that now all 6 spatial dimensions of the two correlated electrons are explicitly considered. The ionisation and electronic excitation is compared for parallel and perpendicular orientation as a function of photon frequency, completely covering the 2- to 5-photon regime (and partly extending into the 1- and 6-photon regimes). Furthermore, two different laser-pulse lengths and intensities as well as two internuclear separations are considered.

For some time it was believed that from an experimental point of view the parallel orientation of  $H_2$  is the most important one, since an intense laser pulse will align the molecule (due to the difference in polarisability parallel and perpendicular to the molecular axis) (1, 24–26). For a sufficiently long laser pulse this alignment will take place during the raising edge of the laser pulse at intensities smaller than the peak intensity at which ionisation occurs. Therefore, the ionisation signal will reflect the ionisation behaviour of a parallel aligned  $H_2$  molecule. However, for very short pulses that are nowadays available even  $H_2$  will not have the time to align to the laser field. In such a case a comparison to experimental data requires the calculation of the ionisation yield of an isotropic or partly aligned sample. Furthermore, short laser pulses with peak intensities too small to cause substantial ionisation are in turn used to generate rotational wave-packets (27, 28). If an ionising laser pulse follows such a pre-pulse with a well-defined time delay, it is possible to control the degree of alignment or even anti-alignment, i. e. to investigate the strong-field behaviour as a function of the expectation value of the angle between the molecular axis and the laser field. This was done for the investigation of the orientational dependence of high-harmonic generation (29) or ionisation, e. g., for molecular nitrogen (30, 31). The latter results motivated corresponding theoret-

ical studies within single-active-electron based strong-field approximations which showed disagreeing and gauge-dependent results for the orientational dependence of the ionisation rate (32–35). Therefore, the investigation of the orientational dependence of the strong-field behaviour based on a full solution of the time-dependent Schrödinger equation is very timely.

## 2. Method

The full-dimensional time-dependent Schrödinger equation (TDSE) is solved by expanding the time-dependent wave function in terms of field-free states. The latter are obtained from a configuration-interaction (CI) calculation in which the Slater determinants are formed with the aid of  $H_2^+$  wave functions expressed in terms of  $B$  splines in prolate spheroidal coordinates ( $1 \leq \xi < \infty$ ,  $-1 \leq \eta \leq 1$ ,  $0 \leq \phi < 2\pi$ ). The electronic structure CI method is discussed in detail in (36). Note, electron-electron interaction is not included in the orbitals used for the CI calculation. Such an approach is especially suitable for asymmetric excited states (for example a state where one electron is left in the lowest lying orbital while the other one is ionised), but is not perfect for describing, e.g., the (symmetric) electronic ground state. Nevertheless, it has been shown in (36) that with the present approach very accurate ground-state energies can be obtained for  $H_2$ , if the basis set is chosen judiciously. In calculations as they are discussed here, a compromise has to be searched for, since the goal is to achieve a rather uniform accuracy with respect to the description of a plethora of states, from the ground state up to very energetic continuum ones.

A key feature of the present approach is the discretisation of the electronic continuum. This is a consequence of the chosen  $B$ -spline basis confined within a finite spatial volume defined by  $\xi_{\max}$ . Therefore, only states that are confined within this volume or that have a node at the volume boundary are obtained (see (36) for a more detailed discussion). Since the code allows to calculate the electronic states of any symmetry (singlet, triplet,  $\Sigma$ ,  $\Pi$ , etc.) it is also possible to perform calculations for any possible orientation of the molecular axis with respect to the polarisation of the laser field. The use of the prolate spheroidal coordinate system allows to solve the electronic problem for arbitrary values of the internuclear distance (37). This is an important advantage over the one-centre approximation. The latter was extensively used for  $H_2$  in theoretical single-photon ionisation studies by F. Martín and collaborators (for a review see (38)). Also previous multi-photon studies on  $H_2$  within LOPT adopted that approach (19, 20). However, the one-centre expansion converges very slowly for large internuclear distances.

The solution of the TDSE describing molecular hydrogen exposed to a laser field follows closely the approach that has successfully been used for one- and two-electron atoms before (see (39) for a review). The total in-field Hamiltonian is given by

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}(t) \quad (1)$$

where  $\hat{\mathcal{H}}_0$  is the field-free electronic Born-Oppenheimer Hamiltonian of a hydrogen molecule and  $\hat{\mathcal{V}}(t)$  is the operator describing its interaction with the (time-dependent) laser field. The non-relativistic approximation is used for both operators, and the interaction with the laser field is described within the dipole approximation and in velocity gauge. For a linearly polarised laser field with the

polarisation axis  $\epsilon$  the interaction operation is given by

$$\hat{\mathcal{V}}(t) = -A(t)\epsilon \cdot \mathbf{P} \quad (2)$$

(Here and in the following atomic units ( $e = m_e = \hbar = 1$ ) are used unless specified otherwise.)  $A(t)$  is the magnitude of the vector potential of the laser field and  $\mathbf{P}$  is the total momentum operator of the electrons.

The present work is restricted to the case where the  $\text{H}_2$  molecule before the pulse is in its ground  $1\Sigma_g^+$  state. For parallel orientation,  $\epsilon \parallel \mathbf{R}$ , only transitions from  $\Sigma_g^+$  to  $\Sigma_u^+$  and vice versa are allowed. Therefore, only two symmetries have to be considered in this case. For perpendicular orientation,  $\epsilon \perp \mathbf{R}$ , the transitions  $\Sigma_g^+ \leftrightarrow \Pi_u \leftrightarrow \Delta_g \leftrightarrow \Phi_u \dots$  are allowed. Moreover, all states with the symmetries  $\Pi, \Delta, \dots$ , i.e. with the absolute value of the component the total angular momentum along the internuclear axis  $\Lambda > 0$ , are double degenerate, since one has for the value of the total angular momentum along the internuclear axis  $M = \pm\Lambda$ . However, the explicit use of the reflection symmetry (here and in the following with reflection the reflection plane containing the molecular axis is meant) helps to reduce the dimensionality of the problem. Indeed, both  $\hat{\mathcal{H}}_0$  and  $\hat{\mathcal{V}}(t)$  are symmetric with respect to the reflection operation and the same is true for the initial  $1\Sigma_g^+$  state. Therefore, only the linear combinations of two degenerate states which are symmetric with respect to the reflection transformation have to be considered. (If the initial state would be  $1\Sigma_g^-$ , the linear combinations had to be antisymmetric.)

The resulting TDSE

$$i \frac{\partial |\Psi\rangle}{\partial t} = \hat{\mathcal{H}} |\Psi\rangle \quad (3)$$

is solved by expanding the wave function  $|\Psi\rangle$  according to

$$|\Psi(t)\rangle = \sum_{n\Omega} C_{n\Omega}(t) |\phi_{n\Omega}\rangle \quad (4)$$

in terms of the time-independent wave functions  $|\phi_{n\Omega}\rangle$ . The latter are solutions of the field-free molecular Schrödinger equation

$$\hat{\mathcal{H}}_0 |\phi_{n\Omega}\rangle = E_{n\Omega} |\phi_{n\Omega}\rangle \quad . \quad (5)$$

The two-electron wavefunctions  $|\phi_{n\Omega}\rangle$  are orthonormal and symmetric with respect to the reflection symmetry. The compound index  $\Omega$  represents  $\Lambda$  and the parity with respect to inversion symmetry (*gerade* or *ungerade*). The  $n$  is just an index of a state with a particular symmetry  $\Omega$ . Due to the chosen approach for solving Eq. (5) (using a CI expansion based on  $\text{H}_2^+$  orbitals that are expanded in a  $B$ -spline basis contained in a finite box) all states are discretised as was mentioned before. Therefore, the index  $n$  remains discrete even for states in the electronic continuum. In the case of perpendicular orientation the summation in Eq. (4) is restricted to  $\Lambda \leq \Lambda_{\text{max}}$ .

Since the CI method (36) generates only solutions  $\psi_{n,\Omega}$  which have  $M = \Lambda$ , they must be adapted for the present purpose. Although for  $\Lambda = 0$  they are equivalent to  $\phi_{n\Omega}$ , for  $\Lambda > 0$  the following linear combination has to be used

$$\phi_{n\Omega} = (\psi_{n,\Omega} + \psi_{n,\Omega}^*)/\sqrt{2} \quad . \quad (6)$$

As discussed in (36), with a proper normalisation of  $\psi_{n,\Omega}$  the reflection transformation is equivalent to a complex conjugation of the wavefunction. Therefore, the definition (6) ensures that  $\phi_{n\Omega}$  is symmetric with respect to reflection.

Substitution of Eq. (4) into the TDSE [Eq. (3)], multiplication of the result by  $\phi_{n'\Omega'}^*$ , and integration over the electronic coordinates yields

$$i \frac{\partial}{\partial t} C_{n'\Omega'}(t) = E_{n'\Omega'} C_{n'\Omega'}(t) + iA(t) \sum_{n\Omega} D_{n'\Omega',n\Omega} C_{n\Omega}(t) \quad (7)$$

with  $D_{n'\Omega',n\Omega} = \langle \phi_{n'\Omega'} | \epsilon \cdot (\nabla_1 + \nabla_2) | \phi_{n\Omega} \rangle$ . As can be shown using Eq. (6), these matrices are related to those obtained in (36),  $\bar{D}_{n'\Omega',n\Omega} = \langle \psi_{n'\Omega'} | \epsilon \cdot (\nabla_1 + \nabla_2) | \psi_{n\Omega} \rangle$ , by the relation

$$D_{n'\Omega',n\Omega} = \begin{cases} \sqrt{2} \bar{D}_{n'\Omega',n\Omega} & \text{for } \Lambda + \Lambda' = 1 \\ \bar{D}_{n'\Omega',n\Omega} & \text{otherwise.} \end{cases} \quad (8)$$

Here, the reality of  $\bar{D}_{n'\Omega',n\Omega}$  and the identity for  $\Lambda > 0$ ,

$$\langle \psi_{n'\Omega'} | \epsilon \cdot (\nabla_1 + \nabla_2) | \psi_{n\Omega}^* \rangle = 0, \quad \text{if } \Lambda' \neq 0 \text{ or } \Lambda \neq 1 \quad , \quad (9)$$

was used.

It should be emphasised that with this approach the complete time dependence is incorporated in the coefficients  $C_{n\Omega}$ . They are calculated by propagating Eq. (7) numerically in time using a variable-order, variable-step Adams solver for ordinary first-order differential equations. The laser-pulse parameters are contained in  $A(t)$ . Different choices for the temporal shape of the pulse are implemented, but in this work only results for  $\cos^2$ -shaped pulses are shown.

For the considered laser parameters converged results were obtained using along the  $\xi$  coordinate 350  $B$  splines of order  $k = 15$  with a linear knot sequence. A box size (defined implicitly by  $\xi_{\max}$  that depends on  $R$ ) of about  $350 a_0$  is chosen for both  $R = 1.4 a_0$  and  $R = 2.0 a_0$ . Along the  $\eta$  coordinate 30  $B$  splines of order 8 were used in the complete interval  $-1 \leq \eta \leq +1$ , but using the symmetry of a homonuclear system as is described in (36). Out of the resulting 5235 orbitals for every symmetry only 3490 orbitals were further used to construct configurations, whereas those orbitals with highly oscillating angular part (with more than 19 nodes for the  $\eta$ -dependent component) were omitted. In most of the subsequent CI calculations approximately 6000 configurations were used for every symmetry. These states result from very long configuration series (3490 configurations) in which one electron occupies the  $\text{H}_2^+$  ground-state  $1 \sigma_g$  orbital while the other one is occupying one of the remaining, e. g.,  $n \pi_u$  or  $n \delta_g$  orbitals. The other configurations represent doubly excited situations and are responsible for describing correlation (and real doubly excited states). To speed up the TDSE calculations an energy cut-off was used as an additional parameter. Only CI states with an energy below this cut-off (in the present case set to about 300 eV) were included in the time propagation. For perpendicular orientation  $\Lambda_{\max} = 3$  (the final number of states used in TDSE calculations is about 21,500) gives sufficient convergence for total yields, as is checked by a comparison to analogous calculations with  $\Lambda_{\max} = 5$  (about 32,000 states).

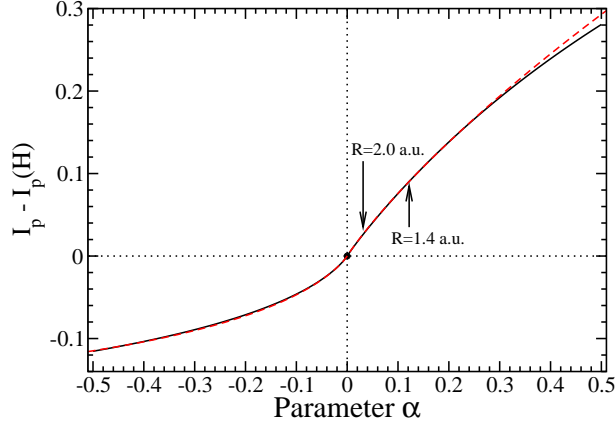


Figure 1. (Color online) Deviation (shift) of the ionisation potential  $I_p$  of the atomic-model potential (10) from its value for  $\alpha = 0$ ,  $I_p(\text{H}) = 0.5 \text{ a.u.}$ , as a function of parameter  $\alpha$ . The dashed line shows the approximation given by the expression (11). The arrows indicate the values of  $\alpha$  used in the present work.

### 3. Atomic model

A molecule treated in the fixed-nuclei approximation differs from an atom due to the anisotropy of the electronic charge distribution which occurs even for the totally symmetric ground state. Alternatively, this anisotropic charge distribution may be described in the language of the linear combination of atomic orbitals (LCAO) as a multi-centre structure that can give rise to interference phenomena. For the analysis of the effects of the anisotropy and thus the corresponding orientational dependence it is therefore of interest to compare the molecular results with the ones obtained for an artificial atom with an isotropic, single-centred charge distribution. Since strong-field ionisation is known to be very sensitive to the electronic binding energy and the exact form of the long-ranged Coulomb potential, it is important that the artificial atom agrees in these properties with the molecule. For this purpose the simple one-parameter model potential

$$V(r) = -\frac{1}{r} \left\{ 1 + \frac{\alpha}{|\alpha|} \exp \left[ -\frac{2r}{|\alpha|^{1/2}} \right] \right\} \quad (10)$$

may be introduced. It satisfies  $V(r) \rightarrow -1/r$  for  $r \rightarrow \infty$  and reduces to the potential of atomic hydrogen,  $I_p(\text{H}) = 0.5 \text{ a.u.}$ , for  $\alpha \rightarrow 0$ . Although the exact ionisation potential  $I_p$  for arbitrary values of the parameter  $\alpha$  can be obtained only numerically, it can be quite well approximated by the following expression

$$I_p(\alpha) \approx I_p(\text{H}) + \frac{\alpha}{(1 + \sqrt{|\alpha|})^s} \quad (11)$$

where  $s = 1$  for  $\alpha > 0$  and  $s = 11/4$  for  $\alpha < 0$ . For  $|\alpha| \ll 1$  the ionisation potential is simply given by  $I_p(\alpha) \approx I_p(\text{H}) + \alpha$ .

Fig. 1 shows the variation of the ionisation potential of the model atom as a function of  $\alpha$ . More precisely, it shows its deviation from the value of the hydrogen atom ( $I_p(\text{H}) = 0.5 \text{ a.u.}$ ). The values of  $\alpha$  used in this work were 0.12194 and 0.03126 (indicated by the arrows in Fig. 1) for simulating an artificial atom with the same ionisation potentials (0.59037 a.u. and 0.52615 a.u.) as the computed ionisation potentials of  $\text{H}_2$  for the internuclear separation of  $R = 1.4 a_0$  and  $R = 2.0 a_0$ , respectively. The dashed line on Fig. 1 shows approximate ionisation potential given by the expression (11), which yields, respectively, 0.59038 a.u. and 0.52656 a.u. for

Table 1. Electronic energies  $E$  (in a.u.) of various  $H_2$  states as they are obtained with the basis sets used in this work and the resulting resonant  $N$ -photon transition frequencies  $\omega$  (in eV) and wavelengths  $\lambda$  (in nm). The last row shows the ground-state energy of  $H_2^+$  and corresponding 1-photon ionisation threshold.

State	$E^a$ , a.u.	$E^b$ , a.u.	$N$	$\omega^a$ , eV	$\omega^b$ , eV	$\lambda^a$ , nm	$\lambda^b$ , nm
1 $^1\Sigma_g^+$ (X)	-1.160351	-1.128787					
2 $^1\Sigma_g^+$ (EF)	-0.690087	-0.716303	2	6.3982	5.6121	193.778	220.922
			4	3.1991	2.8060	387.556	441.844
3 $^1\Sigma_g^+$ (GK)	-0.626453	-0.660305	2	7.2640	6.3739	170.682	194.515
			4	3.6320	3.1870	341.364	389.030
1 $^1\Sigma_u^+$ (B)	-0.702364	-0.745749	1	12.4623	10.4229	99.486	118.953
			3	4.1541	3.4743	298.458	356.859
2 $^1\Sigma_u^+$ (B')	-0.627569	-0.663476	1	14.4975	12.6616	85.520	97.920
1 $^1\Pi_u$ (C)	-0.687338	-0.716903	1	12.8712	11.2078	96.326	110.622
			3	4.2904	3.7359	288.978	331.866
2 $^1\Pi_u$ (D)	-0.623117	-0.654839	1	14.6187	12.8966	84.811	96.136
1 $^1\Delta_g$ (J)	-0.625213	-0.657517	2	7.2808	6.4119	170.286	193.364
2 $^1\Delta_g$ (S)	-0.601098	-0.633603	2	7.6089	6.7372	162.943	184.026
1 $\sigma_g$ [ $H_2^+$ ]	-0.569984	-0.602634	1	16.0645	14.3171	77.178	86.597

<sup>a</sup> For the internuclear distance  $R = 1.4 a_0$

<sup>b</sup> For the internuclear distance  $R = 2.0 a_0$

the values of  $\alpha$  given above.

It should be noted that the model atom is a one-electron (hydrogen-like) atom in which the effect of both the anisotropy due to the two nuclei and due to the second electron in  $H_2$  is solely contained as a screening of the Coulomb potential modifying the ionisation potential. Therefore, this model does not describe any excitation or relaxation of a second electron that can occur in the  $H_2$  calculation. In order to compare to  $H_2$  the atomic results were multiplied by a factor 2 in order to account for the two equivalent electrons in  $H_2$ . This procedure for comparing SAE results with full two-electron calculations were shown to be reasonable (for not too high ionisation yields exceeding about 10 %) in (23).

#### 4. Results

For the subsequent discussion it is helpful to keep in mind the relevant energies and transition frequencies (or wavelengths) of a number of electronic bound states of  $H_2$  that can resonantly be excited by a laser with the corresponding photon frequency. Since the exact positions of the resonances depend on the adopted electronic structure model, Table 1 reports the energies obtained with the present approach and basis set. As was discussed before, the basis set was chosen to provide a good compromise for describing a large number of states and can, of course, not compete with a high-precision calculation optimised for a single electronic state. Furthermore, Table 1 provides the ground-state energy of  $H_2^+$  which allows to calculate the exact position of the different  $N$ -photon thresholds. (The 1-photon threshold is given explicitly.)

Fig. 2 shows the ionisation and electronic excitation yields for  $H_2$  exposed to laser pulses with a total duration of 10 cycles, a peak intensity  $I = 10^{13} \text{ W/cm}^2$ , and a variable photon energy obtained within the fixed-nuclei approximation for the nuclear separation  $R = 1.40 a_0$  that corresponds (to a good approximation) to the equilibrium distance of the field-free  $H_2$  molecule. The excitation yield  $Y_{\text{exc}}$  is defined as the population of all possible electronically bound excited states, i.e.  $Y_{\text{exc}} = 1 - P_{\text{gs}} - Y_{\text{ion}}$  where  $P_{\text{gs}}$  is the population left in the electronic ground state and  $Y_{\text{ion}}$  is the ionisation yield. (Populations and yields are defined in such

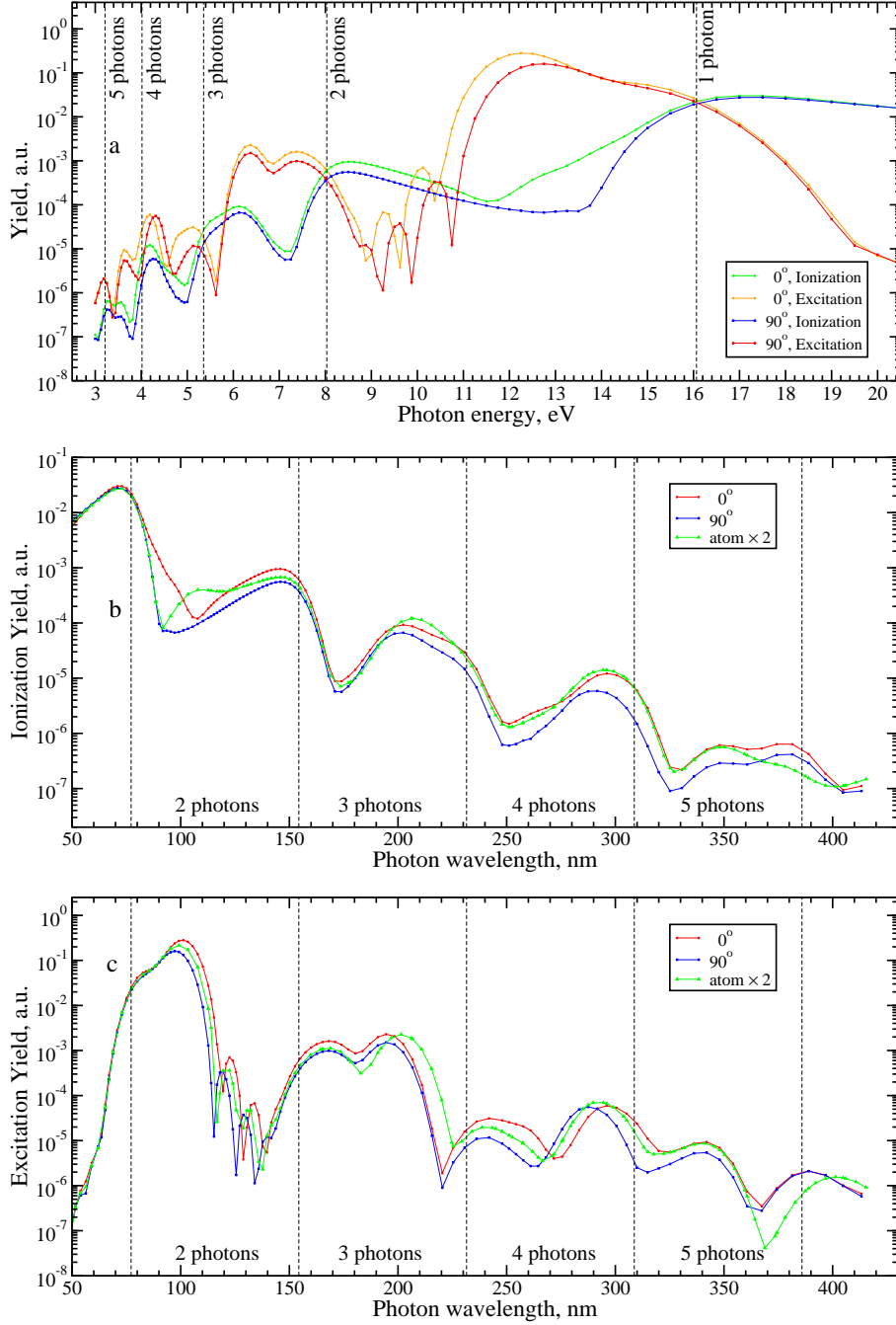


Figure 2. (Color online) Ionisation and excitation yields of an  $\text{H}_2$  molecule with fixed internuclear distance  $R = 1.4 a_0$  for a 10-cycle linear-polarised laser pulse with peak intensity  $10^{13} \text{ W/cm}^2$  and either parallel or perpendicular orientation of the molecular axis with respect to the field. Ionisation and bound-state excitation yields are shown together as a function of the photon energy in eV (a), while b (c) shows the ionisation (excitation) yield as a function of photon wavelength. In the latter cases, also the yields obtained for a model atom (multiplied by a factor 2, see Sec. 3) are plotted. The  $N$ -photon thresholds (for  $N = 1$  to 5) are indicated by vertical dashed lines.

a way that a value of 1 corresponds to 100 %.) The results obtained for a parallel orientation of the molecular axis with respect to the field that are shown in the upper graph agree qualitatively to the ones obtained for different laser parameters (peak intensities were either  $2 \times 10^{12}$  or  $2 \times 10^{14} \text{ W/cm}^2$  and the pulse duration was fixed to 15 fs) in an earlier work (17). However, one notices that the present results are much less structured, despite the larger number of data points and correspondingly higher resolution. Furthermore, the ionisation thresholds marking



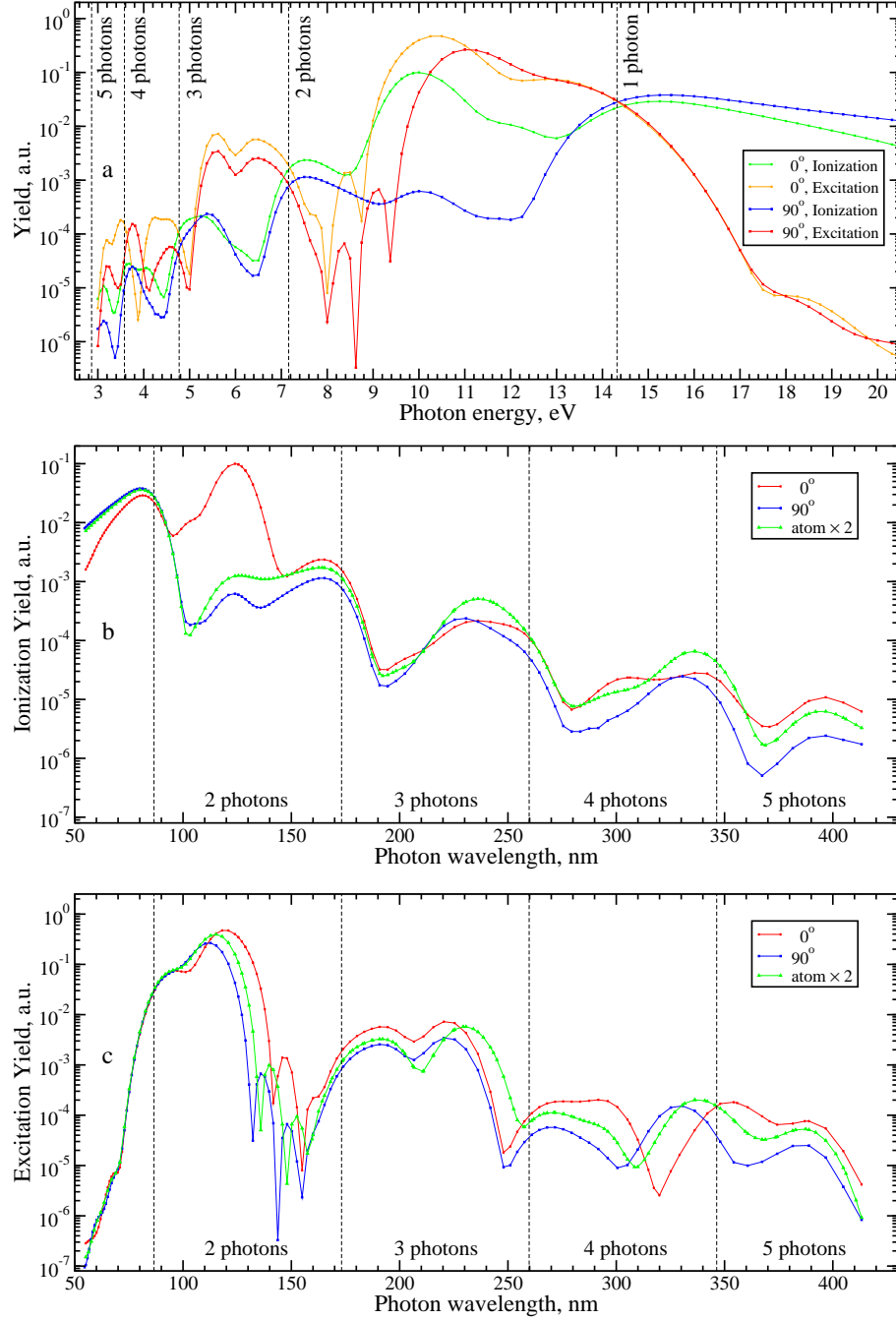


Figure 3. (Color online) As Fig. 2, but for internuclear distance  $R = 2.0 a_0$ .

the transition from an  $N$ - to an  $(N - 1)$ -photon process are by far not as sharp as in (17). This is especially evident for the threshold dividing the 1- and 2-photon ionisation regimes. The reason is the (especially for those large photon energies) much shorter pulse duration of the present 10-cycle pulse compared to a 15 fs pulse used in (17).

A short pulse duration leads to a broad spectral width of the Fourier-limited pulse. Fixing the number of cycles instead of the total pulse duration leads, of course, to a variation of the spectral width as a function of the photon energy. On the other hand, a fixed number of cycles has the advantage that one expects the pulses for different photon energy to become better comparable with respect

to adiabaticity of the process, since a fixed pulse duration can lead in an extreme case to pulses comprising of in one case many and in the other case even less than a single cycle. An effect of the shorter pulse duration can, for example, be seen from the (1+1)-REMPI peaks that are caused by resonant one-photon transitions to the B and the B'  $^1\Sigma_u$  states (cf. Table 1). They are clearly visible in both the excitation and ionisation yields in (17), but appear in Fig. 2a as an almost structureless broad peak in the excitation yield spanning the photon energy range from about 11 to 16 eV. Another remarkable difference to the earlier result obtained for fixed (longer) pulse length is the fact that in this energy window the resonantly enhanced ionisation yield increases almost uniformly with photon energy while in the earlier result there was a pronounced peak at the position of the B state.

In order to substantiate these arguments even more and to provide a more detailed understanding of the influence of the effect of the pulse length on the photon-energy resolved multi-photon spectra, a second series of calculations was performed in which the pulse length was extended to 30 cycles. The results are shown in Fig. 4. Clearly, the ionisation and excitation spectra become much more structured. For example, in the already discussed energy range from 11 to 16 eV one sees now in both the excitation and ionisation yields well separated peaks due to the (1+1)-REMPI process via the B state. Also the B' resonance is clearly visible in the ionisation signal and (though less pronounced) also in the excitation yield. Furthermore, the cut-off due to the closing of the one-photon ionisation channel is much sharper for the 30-cycle pulse — in direct accordance with the smaller band width with which the threshold is convoluted.

One notices also that the 30-cycle pulse leads to a more pronounced REMPI signal, especially for the B state. This reflects the fact that the REMPI process needs some time to occur, since the pulse has to be sufficiently long to first populate and then ionise the resonant intermediate state. Interestingly, the B' state leads to a larger ionisation yield than the B state, although the latter is much more populated. Evidently, the B' state is more easily ionised with the given photon frequency than the B state with the photon energy required for its resonant excitation. All these findings for different pulse lengths underline the need for full time-dependent calculations, if ultrashort pulses are considered.

The excitation spectra in Figs. 4a and c show in the energy range from about 8.5 to 12 eV (100 to 150 nm) a very pronounced oscillatory structure that is absent for the 10-cycle pulses. The origin of this feature is the chosen pulse profile ( $\cos^2$ -type envelope function). Its relatively sharp turn-on and -off (compared to a Gaussian pulse) which is helpful for numerical calculations, since the pulse has a well defined duration leading to a clear interval for the time integration, leads to a corresponding oscillatory behaviour in the energy domain and thus in the convolution function. A semi-quantitative model for this phenomenon may be obtained in the following way. For the given laser intensity and the photon energy required for a resonant transition to the B state (12.46 eV according to Table 1) 1st-order perturbation theory should provide a reasonable approximation for the excitation process. Within lowest-order perturbation theory the rate (and thus for a sufficiently long pulse also the yield) for an  $N$ -photon transition is proportional to  $I^N$  where  $I \propto |F|^2$  is the intensity and  $F$  the corresponding electric field strength. The Fourier component of an  $N_c$ -cycle laser pulse with carrier frequency  $\omega$  (and thus the total pulse duration  $T_p = 2\pi N_c/\omega$ ) at a particular frequency  $\omega_0$  can be obtained from the full time-dependent electric field  $F(\omega, t)$  by a Fourier analysis

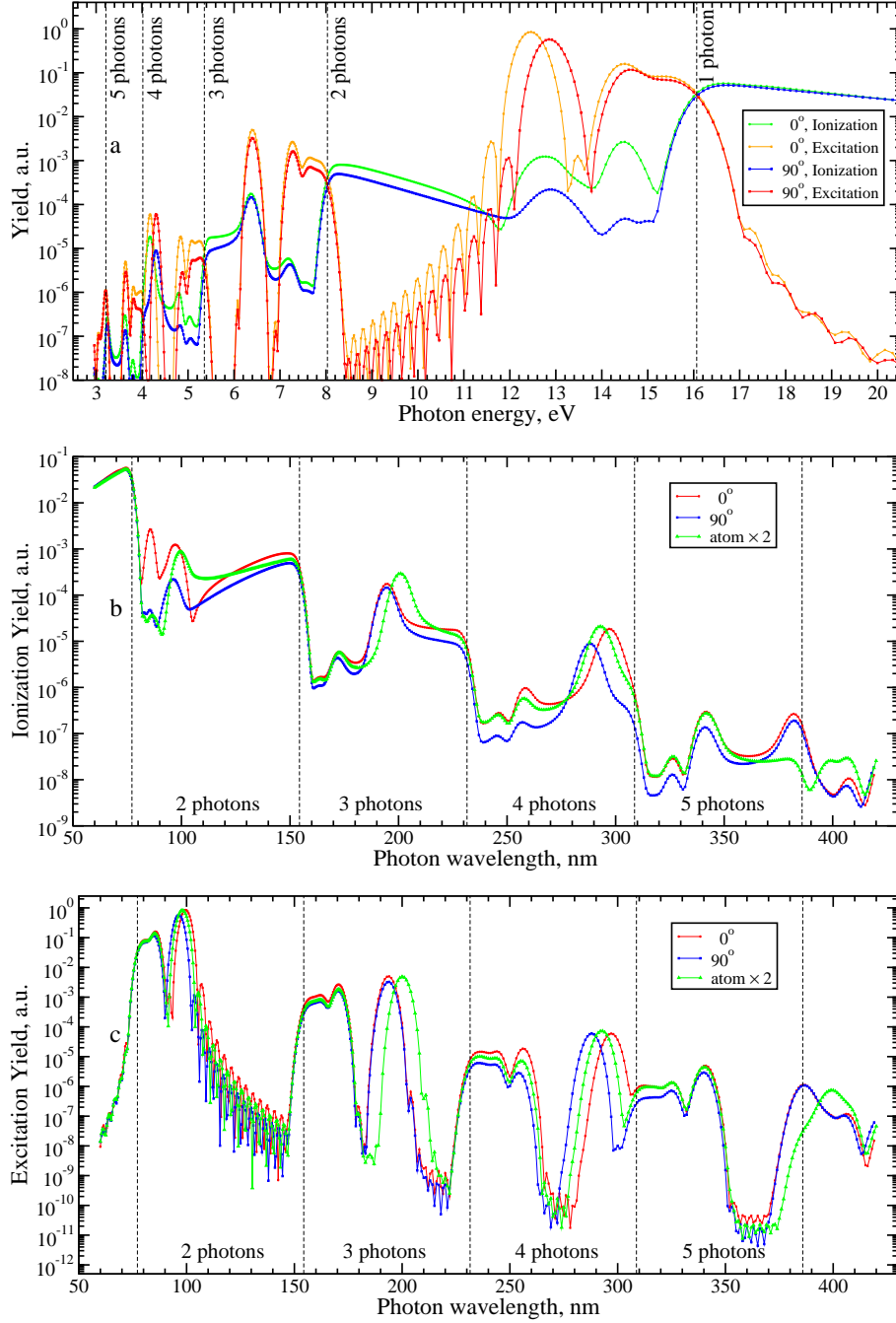


Figure 4. (Color online) As Fig. 2, but for 30-cycle laser pulses with peak intensity  $5 \cdot 10^{12}$  W/cm<sup>2</sup>.

(inverse Fourier transform),

$$F_{\omega_0}(\omega) = \frac{2}{T_p} \int_{-T_p/2}^{T_p/2} dt F(\omega, t) \cos(\omega_0 t) \quad . \quad (12)$$

In Eq. 12 it was used that the  $\cos^2$  laser pulses (with a carrier-envelope phase set to zero) considered in this work lead to an even function  $F(\omega, t)$ . Therefore, the imaginary part of the Fourier transform vanishes.

Within the perturbative model outlined above the resonant 1-photon transition rate to the B-state is convoluted with  $|F_{\omega_0}(\omega)|^2$  where  $\omega_0$  is equal to the transition

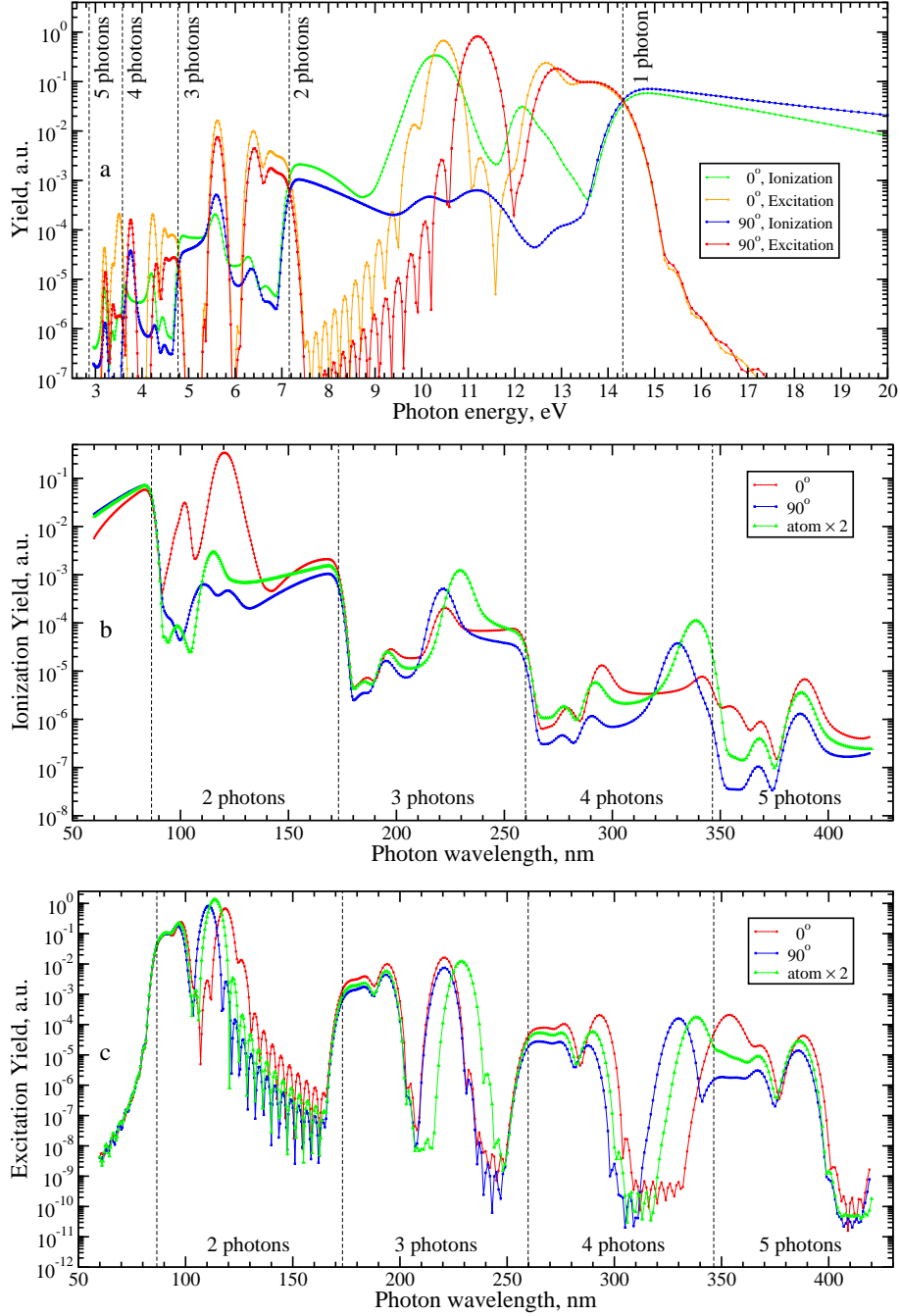


Figure 5. (Color online) As Fig. 4, but for internuclear distance  $R = 2.0 a_0$ .

frequency from the ground state to state B (12.46 eV). Fig. 6 shows this convolution function together with the total excitation rate obtained from the numerical solution of the TDSE. In order to obtain a rate from the calculated excitation yield  $Y_{\text{exc}}$  the approximate relation

$$R_{\text{exc}} \approx -\ln(1 - Y_{\text{exc}})/T_p \quad (13)$$

was used. Clearly, the simple model explains very well the observed oscillatory structure.

Although all sharp features (REMPI peaks or ionisation thresholds) are, of

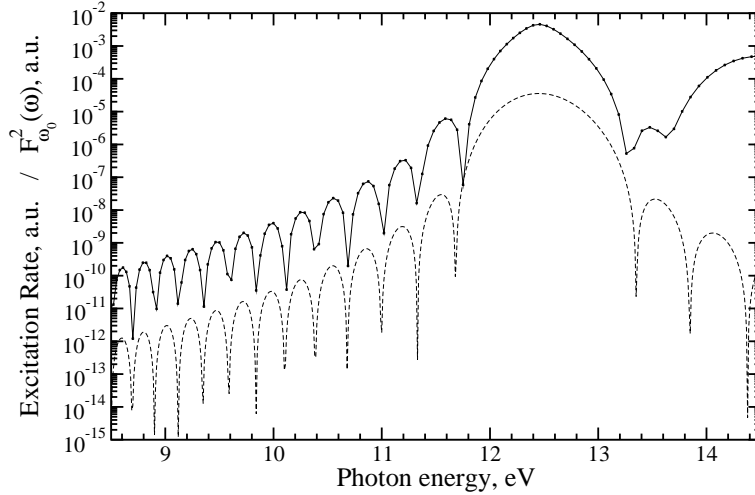


Figure 6. Excitation rate (solid line, extracted from the excitation yield using equation (13)) for an  $H_2$  molecule with fixed internuclear distance  $R = 1.4 a_0$ , a 30-cycle linear-polarised laser pulse with peak intensity  $5 \cdot 10^{12} \text{ W/cm}^2$ , and a parallel orientation of the molecular axis with respect to the field. It is compared with the square of the Fourier component,  $F_{\omega_0}^2(\omega)$  (dashed line, defined in Eq. (12)), where  $\omega_0$  is the transition frequency from state X to state B.

course, convoluted with the same spectral function, the result is only visible if it stems from a very pronounced, i. e. intense and well isolated, signal like the REMPI peak due to the B state. Owing to its very low relative intensity, this structure is in other cases very easily hidden in the background. For example, the oscillations are symmetric around the position of the B-state resonance, but on the high-energy side all but the first side band are completely covered by the excitation yield due to direct transitions to the B' and higher lying Rydberg states. Thus these oscillations are almost only visible in the low-energy side where due to energy conservation no excited state (B is the lowest-lying one) can directly be populated, while the B state can be reached due to the spectral width of the  $\cos^2$ -shaped pulse.

The features and trends discussed above mainly for the 2-photon ionisation regime (including the range of (1+1)-REMPI processes and the 1-photon ionisation threshold) occur also for the other energy ranges considered, but there they are less clearly visible. A better visibility and linearity of the spectrum with respect to the number of photons involved (in a perturbative picture) is obtained, if the yields are shown as a function of the photon wavelength as is done in the middle (lower) panels of Figs. 2 and 4 for the ionisation (excitation) yields. In all considered regimes up to five photons the longer pulses lead to better resolved REMPI peaks and sharper cut-offs at the multi-photon thresholds.

Figs. 2 and 4 show also the results for perpendicular orientation (and  $R = 1.40 a_0$ ). Clearly, the overall spectra look very similar for parallel and perpendicular orientation when a logarithmic scale is used. In the case of 10-cycle pulses both parallel and perpendicular excitation yields show clearly one-photon absorption to the electronic excited states in the energy window of 11 to 16 eV. It is, of course, different electronic states that are excited in the two cases, since the dipole selection rule leads to the excitation of  $^1\Sigma_g$  states for parallel and of  $^1\Pi_u$  states for perpendicular orientation. Noteworthy, the corresponding ionisation yield shows almost no trace of enhancement in this energy window, although the excitation to the lowest lying C state is only a factor 2 to 3 lower than the one to the B state, and the excitation to the higher lying states is practically identical.

For the 30-cycle pulses REMPI peaks become clearly visible in this energy window, but they are much weaker than the corresponding peaks obtained for parallel

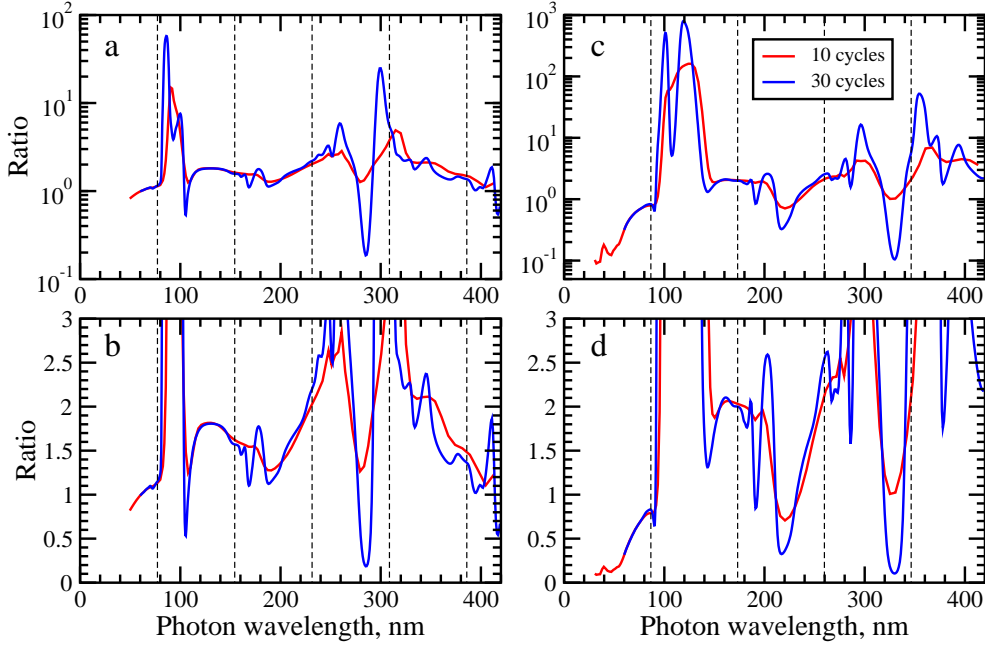


Figure 7. (Color online) Ratio of the ionisation yields for parallel and perpendicular orientation for the internuclear distances  $R = 1.4 a_0$  (a,b) and  $R = 2.0 a_0$  (c,d) on either a logarithmic (a,c) or a linear (b,d) scale. Shown are the results for 10-cycle laser pulses with peak intensity  $10^{13} \text{ W/cm}^2$  (red) and for 30-cycle pulses with peak intensity  $5 \cdot 10^{12} \text{ W/cm}^2$  (blue).

orientation, despite the again very similar excitation yields for the corresponding resonant states. This indicates that the one-photon ionisation of the  $\Pi_u$  states (C, C', etc.) with linear-polarised laser light perpendicular to the molecular axis possesses a much lower probability than the corresponding process for the  $\Sigma_u$  states using parallel orientation. Such a pronounced difference between the resonantly-enhanced ionisation yield and the excitation yield of the resonant state is, however, only observed for the (1+1)-REMPI processes. Already in the 3-photon regime in which (2+1)-REMPI processes occur the ionisation enhancement is to a good approximation proportional to the excitation yield, if REMPI-processes in parallel and perpendicular direction are compared. Within the same orientation (either parallel or perpendicular) the REMPI enhancement is now larger for the dominant excitation peak (at lower energy) than for the one at higher energy.

In fact, as already mentioned, if the region containing (1+1)-REMPI processes is ignored, the parallel and perpendicular ionisation yields are very similar. This is even the case for the excitation yields that are only slightly shifted with respect to each other due to the energy differences of the bound states with different angular momentum  $\Lambda$ . A closer look reveals that apart from the 1-photon regime where parallel and perpendicular yields are almost identical (except the ionisation yields at very high photon energies where perpendicular orientation gives higher yields) the ionisation and excitation yields are rather uniformly larger for parallel than for perpendicular orientation. The ratio between parallel and perpendicular ionisation yields is shown in Fig. 7 a for the 10- and 30-cycle pulses (and  $R = 1.40 a_0$ ). Despite some sharp resonant features that are better resolved for the longer pulses the ratio is rather independent of the pulse duration and varies in between about 1.5 and 2.5 in the whole 2- to 5-photon regime. This overall finding is in reasonable agreement with the corresponding results of 2- and 3-photon lowest-order perturbation theory in (20).

In a recent time-dependent SAE study (22) a rather large deviation to the LOPT result in (20) was found for a photon energy of 10.85 eV ( $\approx 115 \text{ nm}$ ). The ratios

parallel to perpendicular were about 20 (22) or 1.8 (20). As is clearly visible from Fig. 7, the ratio varies rather drastically around this wavelength. The present work gives a ratio of 1.6 at this photon frequency. However, it increases to about 1.8 already at a wavelength of about 120 nm. On the other hand, in between about 115 and 105 nm the ratio drops down to 0.5 before it sharply increases at about 100 nm. As can be especially seen from Fig. 4a, the reason for this pronounced variation of the ratio is the fact that there is a minimum in the ionisation yield for parallel orientation close to this photon energy which may be caused by an interference with the REMPI peak caused by the B state. This minimum together with the REMPI peak that occurs for slightly lower energies than the one due to the C state (perpendicular orientation) leads to the sharp minimum followed by a sharp maximum, if the photon wavelength approaches the region around 125 nm from above. Clearly, depending on the accuracy of the transition energy to the B state provided by a particular electronic-structure model very different results may be obtained for the ratio between parallel and perpendicular orientation at a wavelength around 115 nm.

Similarly, it is difficult to compare to the other recent work discussing orientational dependence of the ionisation behaviour of  $H_2$  within TD-DFT (21). The present results agree to that work in the sense that no pronounced (order-of-magnitude) difference between the parallel and perpendicular orientation is found. However, the results in (21) are either close to saturation of single ionisation (Fig. 4) or the corresponding value at  $R = 1.4 a_0$  is barely readable from the graph (Fig. 5). Furthermore, at the considered wavelength of 266 nm there is some structure due to REMPI peaks. Therefore, the exact result depends again critically on the corresponding excitation energies (and spectral width of the laser pulse). Noteworthy, the present calculation confirms resonant structure at this wavelength as is also noted (for this  $R$  value) in (21).

It is usually assumed that few-photon processes depend heavily on the electronic structure, if not too high intensities are considered, while many-photon processes depend mostly on the ionisation potential and shape of the long-range potential experienced by the ejected electron. Accordingly, one would not expect an atomic model like the one described in Sec. 3 to yield ionisation and excitation yields in reasonable agreement to a full molecular calculation for few-photon processes. However, as is evident from Figs. 2 and 4, the overall agreement even of the excitation yield is in fact surprisingly good. The ionisation yield agrees in the 1-photon regime almost perfectly with the molecular result for perpendicular orientation. Especially for the 30-cycle pulses the agreement continues in the 2-photon regime until the second REMPI peak where the atomic model agrees quantitatively much better with the parallel result. At the threshold between 2- and 3-photon ionisation (at about 155 nm) all three curves agree very well for both pulse lengths. Once the parallel and perpendicular results start to disagree, the atomic result follows now more closely the molecular results for parallel orientation. Starting at about 360 nm the atomic results disagree with the molecular ones that agree at these wavelengths rather well with each other. A very similar result is also found for the excitation yields. This confirms that even the position (and dipole moments) of the excited states are very well approximated by the atomic model proposed in this work.

Finally, it is interesting to investigate whether the findings reported so far apply only to the case when the internuclear distance is relatively small and thus the ground-state electron density is rather isotropic. A second series of calculations was thus performed in which  $R = 2.0 a_0$  was used. The results are given in Figs. 3 and 5 as well as in the right panel of Fig. 7. This choice of  $R$  is motivated by the fact that the ground vibrational wavefunction of  $H_2$  extends to about this distance

and it is at the same time the equilibrium distance of the  $\text{H}_2^+$  ion created in the ionisation process.

Most evidently, the 1- and 2-photon ionisation yields disagree for the two orientations much more than for  $R = 1.40 a_0$ . Only at the threshold between the two regimes reasonable to good agreement is found. While the 1-photon yield for parallel orientation lies below the perpendicular one, this changes drastically in the 2-photon regime. The latter difference seems to be mainly due to the now even much more pronounced REMPI peaks for parallel orientation. Noteworthy, the excitation yields are very similar for the two orientations, besides the energy shifts due to different excitation energies. In the regimes of 3- to 5-photon ionisation the qualitative difference between the two orientations is less pronounced than in the 2-photon case. Compared to  $R = 1.4 a_0$  it is especially the quantitative agreement between the two orientations which becomes worse, if  $R$  increases. This is also seen from the corresponding ratio (Fig. 7) which covers a larger range of values in this case. It is also interesting to note that a comparison of the results for  $R = 1.4$  and  $2.0 a_0$  shows that there is quite good qualitative agreement. The main difference is that with increasing  $R$  value the excitation energies become smaller. Together with a decrease of the vertical ionisation potential when going from  $R = 1.4$  to  $2.0 a_0$  this leads to an effective compression of the wavelength ranges for a given  $N$ -photon regime. The, of course,  $R$ -independent results of the atomic model agree not as well with the molecular yields for larger than for smaller  $R$ , as is expected. Nevertheless, the atomic model still works reasonably well for a qualitative or even semi-quantitative estimate.

## 5. Conclusion and outlook

A previously developed numerical approach for solving the time-dependent Schrödinger equation that describes the correlated motion of both electrons of molecular hydrogen exposed to a short intense laser pulse in the non-relativistic, fixed-nuclei, and dipole approximation has been extended to consider also a perpendicular orientation of the molecular axis with respect to the laser field. The ionisation and excitation yields were calculated for photon wavelengths of about 40 to 420 nm covering the complete 2- to 5-photon regime and extending into the 1- and 6-photon ranges. Two pulse lengths (10- or 30-cycle pulses) and two internuclear separations ( $1.4$  and  $2.0 a_0$ ) were considered.

Mainly due to the smaller spectral width (but partly also due to the lower peak intensity), the longer pulses yield much more structured spectra than the short ones. However, due to the intrinsic time dynamics of the REMPI process as a consequence of the implied two-step process (population and depopulation of the resonant state), the different REMPI signals show a different pulse-length dependence.

It is found that the parallel and perpendicular spectra agree qualitatively quite well with each other, the main difference stems from the difference in the positions of the resonant peaks due to the different symmetries of the corresponding intermediate states. Even the quantitative differences are not too large in the non-resonant parts of the spectra. At the equilibrium distance of  $\text{H}_2$  the ratio of parallel to perpendicular non-resonant multi-photon ionisation yields varies in between 1 and 2.5. It is therefore only weakly anisotropic. For the increased distance  $2.0 a_0$  this ratio tends especially in the 4- and 5-photon regimes to slightly larger values up to about a value of 4. The ratios found in the 2- and 3-photon regimes agree reasonably well with previous ones obtained with perturbation theory (20), but



disagree with the much larger value obtained at a single photon frequency in the 2-photon regime using a single-active-electron approximation (22). However, very large ratios are found in the resonant regimes. Since the position of the resonances depends on the quality of the used electronic-structure model, large discrepancies may occur, if different levels of approximation are used.

An atomic model is proposed that allows to easily tune the ionisation potential while maintaining asymptotically the shape of the appropriate long-ranged Coulomb potential. This allows to more clearly analyse molecular effects that are caused by the multi-centred character of a molecular electron density. Surprisingly, even (in fact especially) in the few-photon regime the single-electron atomic model compares very well with both the ionisation and excitation yield obtained with the full molecular two-electron calculation.

Presently, this work is extended to longer wavelengths (especially the popular 800 nm of the Ti:sapphire laser) and to the analysis of differential quantities like above-threshold-ionisation (ATI) electron spectra. Furthermore, the anisotropy of high-harmonic emission of  $H_2$  will be investigated.

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